

### **IN THE SPECIFICATION**

Amend the specification as follows:

Please substitute the following clean-text paragraph for the paragraph beginning on page 1, line 6:

This application is a Divisional of U.S. patent application entitled “Silicon Based Nanospheres and Nanowires”, filed on March 29, 2001 and assigned serial number 09/820,413, which claimed the benefit of U.S. Provisional application entitled, “Silicon Based Nanowires and Nanospheres”, filed on March 29, 2000, and assigned Serial No.: 60/192,846, and U.S. Provisional application entitled “New Cu/SiO<sub>2</sub> Based Catalyst for Selective Ethanol-Acetaldehyde Conversion”, filed on March 29, 2000, and assigned Serial No.; 60/192,844, which are both entirely incorporated herein by reference.

**Please insert the following pages for the pages of the same number in the application:**

The following is a marked up version of the amended specification. Amend the following specification by adding the language that is underlined (“    ”) and by deleting the language that is enclosed within brackets (“[ ]”):

Page 4

methods, features, and advantages be included within this description, be within the scope of the present invention, and be protected by the accompanying claims.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Many aspects of the invention can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale, emphasis instead being placed

upon clearly illustrating the principles of the present invention. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

FIG. 1 illustrates a cross-sectional view of a representative embodiment of a nanosphere and a nanowire.

FIG. 2 illustrates a flow diagram of a method for producing a nanostructure.

### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT**

Embodiments of the present invention provide for nanostructures 10, catalytic nanostructures, and methods of preparation of same, as shown in FIGS. 1 and 2. Nanostructures 10 include, but are not limited to, nanowires 14, nanospheres 12, nanoagglomerates, nanotubes, *etc.* More specifically, exemplary embodiments of the present invention provide a nanowire 14 and methods of preparation thereof. Another exemplary embodiment provides a nanosphere 12 and methods of preparation thereof. Still another exemplary embodiment provides a catalytic nanosphere and methods of preparation thereof (*e.g.*, a metallized nanosphere with catalytic activity). The nanostructures 10 can be made [of] from materials such as, but not limited to, metals, metal oxides, metalloids, metalloid oxides, combinations of metals, combinations of metal oxides, combinations of metalloids, combinations of metalloid oxides, combinations of metals and metal oxides, combinations of metalloid and metalloid oxides, or any other appropriate combination. The nanostructures 10 can be made of materials such as, but not limited to, metal oxides and metalloid oxides. Further, the nanostructures 10 can be metallized to form catalytic nanostructures that can be used to enhance reaction kinetics and reaction efficiency.

#### **A. Nanowires and Nanospheres**

One exemplary embodiment of the present invention provides for a nanowire prepared under thermal and non-catalytic conditions. The thermal conditions include, but are not limited to, the range of 800°C to 1500°C. The term non-catalytic conditions means, for the purposes of this disclosure, that an additional catalyst is unnecessary for the nanostructures to be fabricated.

In an exemplary embodiment, the nanowire can be fabricated [to form] from metal, metal oxide, metalloid, metalloid oxide, or combinations thereof, to form metal oxide or metalloid oxide nanowires.

In a preferred embodiment, the nanowires include silicon dioxide sheathed crystalline silicon nanowires where the axis of the crystalline silicon nanowire core is substantially parallel to a  $\langle 111 \rangle$  plane. In addition, the silicon nanowires are substantially

defect free. That is, the silicon nanowires are substantially free of twinning, high order grain boundaries, and stacking faults.[

]Non-limiting examples of metals from which the nanowires can be fabricated include, but are not limited to, tin (Sn), chromium (Cr), iron (Fe), nickel (Ni), silver (Ag), titanium (Ti), cobalt (Co), zinc (Zn), platinum (Pt), palladium (Pd), osmium (Os), gold (Au), lead (Pb), iridium (Ir), molybdenum (Mo), vanadium (V), aluminum (Al), or combinations thereof. In addition, non-limiting examples of metal oxides from which the nanowires can be fabricated [into] include, but are not limited to, tin dioxide ( $\text{SnO}_2$ ), chromia ( $\text{Cr}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , or  $\text{FeO}$ ), nickel oxide ( $\text{NiO}$ ), silver oxide ( $\text{AgO}$ ), titanium oxide ( $\text{TiO}_2$ ), cobalt oxide ( $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , or  $\text{CoO}$ ), zinc oxide ( $\text{ZnO}$ ), platinum oxide ( $\text{PtO}$ ), palladium oxide ( $\text{PdO}$ ), vanadium oxide ( $\text{VO}_2$ ), molybdenum oxide ( $\text{MoO}_2$ ), lead oxide ( $\text{PbO}$ ), and combinations thereof. In addition, [a] non-limiting [example] examples of [a metalloid] metalloids from which the nanowire can be fabricated [includes] include, but [is] are not limited to, silicon or germanium. Further, [a] non-limiting [example] examples of [a] metalloid [oxide] oxides from which the nanowire can be fabricated [includes] include, but [is] are not limited to, silicon monoxide, silicon dioxide, germanium monoxide, and germanium dioxide. The nanowire can be a metal oxide or metalloid oxide nanowire.

Another exemplary embodiment of the present invention provides for a plurality of nanospheres that are substantially monodisperse and a method of preparation thereof. In addition, the nanospheres can be fabricated in gram quantities under thermal and non-catalytic conditions. The thermal condition includes, but is not limited to, the range of  $800^\circ\text{C}$  to  $1500^\circ\text{C}$ . The term non-catalytic conditions means that an additional catalyst is unnecessary for the nanostructures to be fabricated. Further, the nanospheres can be fabricated [to form metal] from, metal oxide, metalloid, metalloid oxide, or combinations thereof nanospheres.[

]Non-limiting examples of metals from which the nanospheres can be fabricated include, but are not limited to, tin (Sn), chromium (Cr), iron (Fe), nickel (Ni), silver (Ag), titanium (Ti), cobalt (Co), zinc (Zn), platinum (Pt), palladium (Pd), osmium (Os), gold (Au), lead (Pb), iridium (Ir), molybdenum (Mo), vanadium (V), aluminum (Al), and combinations thereof. In addition, non-limiting examples of metal oxides from which the nanospheres can be fabricated include, but not limited to, tin dioxide ( $\text{SnO}_2$ ), chromia ( $\text{Cr}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , or  $\text{FeO}$ ), nickel

Page 5 Cont.

oxide (NiO), silver oxide (AgO), titanium oxide (TiO<sub>2</sub>), cobalt oxide (Co<sub>2</sub>O<sub>3</sub>, Co<sub>3</sub>O<sub>4</sub>, or CoO), zinc oxide (ZnO),

platinum oxide (PtO), palladium oxide (PdO), vanadium oxide (VO<sub>2</sub>), molybdenum oxide (MoO<sub>2</sub>), lead oxide (PbO), and combinations thereof. In addition, [a] non-limiting [example] examples of [a metalloid] metalloids from which the nanospheres can be fabricated [includes] include, but is not limited to, silicon and germanium. Further, [a] non-limiting [example] examples of [a] metalloid [oxide] oxides from which the nanospheres can be fabricated [includes] include, but [is] are not limited to, silicon monoxide, silicon dioxide, germanium monoxide, and germanium dioxide.[

]In general [The] the nanospheres can range in diameter from a few nanometers to on the order of hundreds of nanometers. More particularly, silicon dioxide nanospheres are amorphous, have no dangling bonds, and range in diameter from about 8-45 nanometers (nm). Further, the method of fabricating nanospheres and nanowires using thermal techniques can be similar. In this regard, both nanospheres and nanowires can be fabricated using similar fabrication steps. Modifications in fabrication parameters, disclosed hereinafter, can be used to control the quality and quantity of the fabricated nanospheres and nanowires.

For the purposes of illustration only, and without limitation, embodiments of the present invention will be described with particular reference to the below-described fabrication methods. Note that not every step in the process is described with reference to the process described in the figures hereinafter. Therefore, the following fabrication processes are not intended to be an exhaustive list that includes every step required to fabricate the embodiments of the nanostructures.

FIG. 2 illustrates a flow diagram of a representative method 20 for producing the nanostructure 10 (e.g., nanowires 12 and nanospheres 14). In block 22, at least one composition, such as those described above, is provided. In block 24, the composition is vaporized. In block 26, the nanostructure 10, such as those described above, is formed via a condensation reaction under non-catalytic conditions.

### **Example 1**

The following is a non-limiting illustrative example of an embodiment of the present invention that is described in more detail in *Gole, et al.*, Appl. Phys. Lett., 76, 2346 (2000), which is incorporated herein by reference. This example is not intended to limit the scope of any

embodiment of the present invention, but rather is intended to provide specific experimental conditions and results. Therefore, one skilled in the art would understand that many experimental conditions can be modified, but it is intended that these modification are within the scope of the embodiments of the present invention.

The apparatus to fabricate silicon based nanostructures includes a double concentric alumina tube combination that can be heated to the desired temperature in a Lindberg Scientific tube furnace configuration. The inner alumina tube is vacuum sealed by two water cooled stainless steel end pieces which are attached to the alumina tube and tightly lock-press fit against custom viton o-rings. At one end of the furnace, ultra-high purity argon (Ar) enters through the upstream stainless steel end piece and passes through a matched set of zirconia insulators to the central region of the inner tube oven. Here the entraining argon flows over a crucible containing the sample mixture of interest, which may be either a silicon-silica ( $\text{Si/SiO}_2$ ) mixture or powdered silicon monoxide, at a flow

**Please amend the paragraph starting on p. 7, line 22 as follows:**

In an exemplary embodiment, virtually uniform and straight nanowires were generated from a 50/50 Si/SiO<sub>2</sub> equimolar mixture heated to a temperature of about 1400°C at a total pressure of about 225 Torr for about 12 hours. The central crystalline silicon core for the nanowire is about 30 nm in diameter, whereas the outer SiO<sub>2</sub> sheathing is about 15 nm in thickness, as exemplified in *Gole et al.*, Appl. Phys. Lett., 76, 2346 (2000), which is incorporated herein by reference. However, nanowires with much smaller and larger diameter central crystalline cores and different sheathing thickness have been obtained. The axis of the SiO<sub>2</sub> clad crystalline silicon nanowire core is substantially parallel to the  $\langle 111 \rangle$  plane. This is distinct from the results obtained by *Lee et al.*, MRS Bulletin, 36 (1999) whose wires have their axis parallel to  $\langle 112 \rangle$  plane as they display twinning, high order grain boundaries, and stacking faults. At the Si-SiO<sub>2</sub> interface for the material obtained in the present synthesis the crystal planes are best described as  $\langle 211 \rangle \{211\}$ . The nanowires synthesized are so perfect that slight undulations of the crystalline silicon core, due to strain induced by measuring devices, can be observed.

**Please amend the paragraph starting on p. 8, line 29 as follows:**

Judicious manipulation of the high temperature system including reactant mixture stoichiometry, flow conditions (kinetics), and temperature range, may yield more than would have been previously anticipated by others skilled in the art. The results suggest that additional mechanisms which are analogs not only of the VLS mechanism on the nanoscale but also represent some crystalline silicon self-assembly may be operative. Further, *Lee et al.* produce a jumble of uniform SiO<sub>2</sub> coated crystalline silicone nanowires of various sizes which, when straight, have their axes parallel to  $\langle 112 \rangle$ . These wires, however, display ~~twinning~~ ~~twinning~~, high order grain boundaries, and defect sites (stacking faults). In contrast, embodiments of the present invention are capable of producing nanowires where the axis of the nanowire core is substantially parallel to a  $\langle 111 \rangle$  plane, virtually defect free, and demonstrate no ~~twinning~~ ~~twinning~~. Given the high temperature synthesis of alternate combinations of metal/metal oxide nanowire configurations, embodiments of the present invention appear to be well suited to photonic waveguide applications.



**Please amend the paragraph starting on p. 9, line 23 as follows:**

Non-limiting examples of metals from which the nanospheres can be fabricated include, but are not limited to, tin (Sn), chromium (Cr), iron (Fe), nickel (Ni), silver (Ag), titanium (Ti), cobalt (Co), zinc (Zn), platinum (Pt), palladium (Pd), osmium (Os), gold (Au), lead (Pb), iridium (Ir), molybdenum (Mo), vanadium (V), aluminum (Al), and combinations thereof. In addition, non-limiting examples of metal oxides from which the nanospheres can be fabricated include, but are not limited to, tin dioxide ( $\text{SnO}_2$ ), chromia ( $\text{Cr}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , or  $\text{FeO}$ ), nickel oxide ( $\text{NiO}$ ), silver oxide ( $\text{AgO}$ ), titanium oxide ( $\text{TiO}_2$ ), cobalt oxide ( $\text{Co}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ , or  $\text{CoO}$ ), zinc oxide ( $\text{ZnO}$ ), platinum oxide ( $\text{PtO}$ ), palladium oxide ( $\text{PdO}$ ), vanadium oxide ( $\text{VO}_2$ ), molybdenum oxide ( $\text{MoO}_2$ ), lead oxide ( $\text{PbO}$ ), and combinations thereof. In addition, ~~[[a]] non-limiting examples example of [[a]] metalloids include metalloid includes~~, but are is not limited to, silicon and germanium. Further, ~~[[a]] non-limiting examples example of a metalloid oxides include oxide includes~~, but are is not limited to, silicon monoxide, silicon dioxide, germanium monoxide, and germanium dioxide. The nanospheres can range in diameter. More particularly, silicon dioxide nanospheres are amorphous, have no dangling bonds, and range in diameter from about 8-45 nanometers.

**Please amend the paragraph starting on p. 11, line 29 as follows:**

TEM micrographs indicate that nearly monodisperse  $\text{SiO}_2$  nanospheres of diameter of close 30 nm can be generated in gram quantities on the cold plate of the high temperature synthesis device described earlier. As described earlier, the apparatus includes a double concentric alumina tube combination heated to the desired temperature in a Lindberg Scientific tube furnace configuration. The inner alumina tube is vacuum sealed by two water cooled stainless steel end pieces which are attached to the alumina tube and tightly lock-press fit against custom viton™ o-rings. At one end of the furnace, ultra high purity argon enters through ~~thru~~ the upstream stainless steel end piece and passes through a matched set of zirconia insulators to the central region of the inner tube oven. The entraining argon then flows over a crucible containing the sample mixture of interest, which is either a silicon-silica ( $\text{Si/SiO}_2$ ) mixture or powdered silicon monoxide, at a flow rate of 100 sccm controlled a flow controller.

**Please amend the paragraph starting on p. 12, line 25 as follows:**

The Cu/silica catalysts were prepared through batch impregnation of 1 g of the silica with sufficient  $\text{Cu}(\text{AcAc})_2$  metal complex to produce a sample having 3 wt% Cu. The complex was added to 25 mL of acetonitrile solvent and allowed to reflux with stirring for 24 h. The solid was separated by filtration and dried at room temperature for 18 hours [[h]]. This solid was dried at 100°C for 1 hour then placed in a microreactor tube.

**Please amend the paragraph starting on p. 13, line 1 as follows:**

The ethanol dehydrogenation reaction was completed in a micro-catalytic reactor. Prior to the reaction, the nanosphere catalyst was heated to about 350°C for about 1 hour [[h]] in flowing helium, then cooled to the reaction temperature. The reaction conditions were conducted at about 330°C, 20 mL per minute of He carrier gas flow over a 100 mg bed of catalyst having a Cu loading of 3 weight percent. Five to ~~ten~~ ten pL pulses of ethanol were vaporized into the He carrier gas stream to create the reactant feed. Pulses of unreacted ethanol and the products of reaction were partitioned on a GC column and detected by a thermal conductivity detector.

**Please amend the paragraph starting on p. 13, line 25 as follows:**

Flame-hydrolyzed, amorphous silica shows a signature for the SiO-H vibration near 3743  $\text{cm}^{-1}$  and a broad peak near 3400  $\text{cm}^{-1}$  that corresponds to absorbed ~~adsorbed~~ water. Additionally, Si-O vibrations are evident at 1800 and 1600  $\text{cm}^{-1}$ . It appears that the surface functional groups found on the silica nanospheres are similar to those found to be present on Cab-O-Sil™.